

# Automated Technique for Mercury Determination at Sub-nanogram per Litre Levels in Natural Waters\*

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**A sensitive and automatic technique for dissolved mercury determination has been developed in order to produce rapid and accurate dissolved mercury determinations in natural waters at ambient levels. This is needed for building realistic mass balance budgets and providing more accurate data in monitoring programmes for this metal. The detection limit obtained with a 45 ml sample was  $0.1 \text{ ng l}^{-1}$ . The precision of the method over the range  $0.5\text{--}50 \text{ ng l}^{-1}$  was found to be approximately 5%. Eight samples per hour can be analysed without carryover effects. The instrumentation is very robust but strict control measures are required to ensure a mercury-free environment around the instrumentation.**

**Keywords:** *Mercury; cold vapour; atomic fluorescence spectrometry; water*

Over the last decade investigations to determine mercury in natural waters have established that the typical total dissolved mercury concentration (*i.e.*, inorganic and organic species in solution) are at the picomolar level ( $0.2\text{--}100 \text{ ng l}^{-1}$ ) and in some cases even lower.<sup>1-4</sup> In oceanic surface waters, the concentration can be lower than the detection limit generally obtained in this type of ultra trace analysis, namely  $0.05 \text{ ng l}^{-1}$ .<sup>3-5</sup> Concentrations can reach  $2 \text{ ng l}^{-1}$  in the intermediate water layers of the oceans.<sup>5-8</sup> In freshwater systems, the concentration range seems to be larger;  $0.5\text{--}100 \text{ ng l}^{-1}$  as total dissolved mercury in pristine and contaminated Californian lakes,<sup>4</sup> and  $0.5\text{--}6.4 \text{ ng l}^{-1}$  as total dissolved mercury in rivers [ $0.6\text{--}1.1 \text{ ng l}^{-1}$  in the Lena River (Siberia) near its delta out-flowing in the Arctic Ocean far from human activities<sup>9</sup> and  $0.5\text{--}6.4 \text{ ng l}^{-1}$  on the heavily industrialized Seine River (France) during the first year of a monitoring programme].<sup>10</sup>

Despite these major advances in the knowledge of the range of concentrations of mercury in natural waters, the behaviour of this metal in the environment is still poorly understood. High resolution vertical distributions of mercury concentrations in the oceans, seas and coastal zones, and temporal variations in freshwater systems are needed for a better understanding of its geochemical pathways and for building realistic mass balance budgets. In addition to these scientific needs, there is a tendency, within the regulatory agencies, towards

requirements of better detection limits for dissolved mercury determinations in monitoring programmes. This is particularly the case for the accurate assessment of the temporal trends in riverborne mercury inputs to the coastal zones required by international conventions. Therefore a sensitive and automatic technique for dissolved mercury determination in water would be very helpful.

Recently Stockwell *et al.*<sup>11</sup> proposed a fully automated system for the determination of mercury at very low levels in environmental samples. This system consists of a random access autosampler (PSA 20.099), a continuous flow vapour generator (PSA 10.003) which converts the dissolved mercury (II) into elemental mercury using a reducing agent. Mercury vapour is then stripped from the liquid through a phase separator using an argon carrier gas and collected on a gold platinum trap (PSA 10.501 Galahad); on heating the trap the mercury is re-vaporized into an atomic fluorescence detector (PSA 10.023 Merlin) by means of an argon gas stream. The different analytical steps are controlled by a computer using the PSA TouchStone (M023T150) software package which also processes analogue data. The combination of the preconcentration step on a gold platinum trap and the utilization of atomic fluorescence detection maximizes the sensitivity of the mercury determination. However, until now, reagent blanks and blanks originating from carrier gas streams have constantly been introduced into the gold platinum trap and therefore the limit of detection was limited to the nanogram per litre range.

Consequently, PSA have developed a vapour generator (PSA 10.004) which has complete flexibility in terms of valve time sequencing. Previously the valve sequence was operated by the control panel on the vapour generator, which only allowed a predesignated selection of times. The new system is computer controlled, allowing the introduction of sample volumes between 0.03 and 9000 ml. This flexibility allows discrete samples to be introduced in a flow injection type manner. Corns *et al.*<sup>12</sup> have used this approach to extend the linearity of the atomic fluorescence system up to  $10 \text{ mg l}^{-1}$ , and to overcome matrix interferences. When the valve is opened for a longer duration, greater sample volumes are introduced, allowing accurate preconcentration measurements.

The vapour generator activates the valve sequence for the amalgamation unit (PSA 10.501S Galahad). This effectively diverts the mercury gas over the gold platinum trap only during the sample introduction period. The automated system is described in detail for the determination of mercury in natural waters.

\* Presented at the Seventh Biennial National Atomic Spectroscopy Symposium (BNASS), Hull, UK, July 20-22, 1994.

## EXPERIMENTAL

### Reagents

Unless otherwise specified, all reagents were of Suprapur grade (Merck). De-ionized water obtained with a MilliRO4 system (Millipore, Bedford, MA, USA) was used throughout. The reductant solution used was a tin(II) chloride (10% m/v in 20% hydrochloric acid) solution. This solution was continuously purged with mercury-free nitrogen ( $100 \text{ ml min}^{-1}$ ) during the running of the operation to maintain low mercury contamination. The reductant solution was prepared daily. Standard solutions were prepared by appropriate dilution of the stock  $1000 \text{ mg l}^{-1}$  mercury(II) solution. Fresh solutions were prepared daily.

### Instrumentation

#### Continuous flow vapour generator

The high precision peristaltic pump (Labcraft, Armtop, Saint-Andre-des-eaux, France) drives the water sample at a flow rate of  $9 \text{ ml min}^{-1}$  and the reducing solution at the nominal flow rate of  $0.4 \text{ ml min}^{-1}$ . When activated, the unit goes through a cycle involving four stages: (i) delay, the time required for the sample to reach the switching valve; (ii) rise, the time for the signal to reach a steady state; (iii) analysis, period in which signal is at steady state; and (iv) memory, the time for the signal to decay to the baseline. In this study a delay of 35 s was selected. This ensured complete washout of the sample lines between samples. The rise time was set to 30 s and the analysis time to 5 min. The combined time for this stage of the cycle dictates the sample volume which is preconcentrated. The time for the signal to reach baseline was found to be 60 s.

#### Gas-liquid separator

A new gas-liquid phase separator was designed to increase the sensitivity of the mercury detection system. A five-fold increase in sensitivity enhancement was obtained by purging the mercury out of the reaction vessel more efficiently per unit flow of argon. This was achieved by using a very fine glass sinter for the gas supply. An illustration of the device is shown in Fig. 1. The gas-liquid separator was optimized for maximum perform-

ance and an optimal flow rate of  $50 \text{ ml min}^{-1}$  was obtained. This gas flow maximizes the collection efficiency during the amalgamation.

#### Amalgamation device

The amalgamation column consists of a 2 cm length of gold platinum gauze maintained in a quartz tube held in position by a simple restriction. Around the trap is a Nichrome coil, which is in turn connected to the power supply. Both the coil and the trap are retained in a specially designed cooling chamber. This allows visual inspection of the coil and trap and allows a cooling gas to pass over the coil to reduce the temperature rapidly, and allow the next sample to be collected. The cooling gas flow of either nitrogen, argon or air is simply vented to waste.

Once the mercury has been collected on the gold column the amalgamation unit goes through three timed cycles: (i) flush, the time for residual sample gases to be flushed out of the sample lines; (ii) vaporize, the time the gold trap is heated to release mercury into the fluorescence detector; and (iii) cooling, the time to cool the trap to room temperature and thus allow collection of the next sample.

In this study the flush time was 30 s. All mercury trapped was found to be released in 20 s and the time to cool the trap was 90 s. The argon flow rate through the gold trap to the fluorescence detector was  $80 \text{ ml min}^{-1}$  during the measurement. With this configuration it is possible to optimize the flows for preconcentration and for re-vaporization.

#### Atomic fluorescence detector

The atomic fluorescence detector consists of a high intensity dc mercury vapour discharge lamp, a series of lenses and collimating devices to focus and collect light with minimization of scatter, a 254 nm interference filter to achieve wavelength isolation and a conventional side window photo multiplier tube (IP28, Hamamatsu). Essentially, light from the source is collected using a biconvex quartz lens and focused light is collimated into the atom cell. Opposite the lamp is a small photo diode reference cell. The fluorescence emission is detected after collimation and wavelength isolation. The detector may operate in either emission or ratio mode. The emission mode corresponds to the direct atomic fluorescence measurement. The ratio mode corresponds to the reference signal divided by

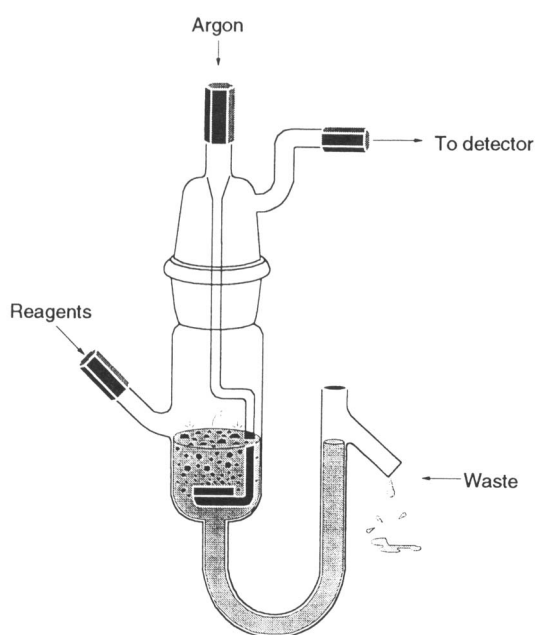


Fig. 1 Gas-liquid separator with sinter

Table 1 Summary of conditions for continuous flow vapour generation-gold amalgamation-atomic fluorescence spectrometry (AFS)

Parameter	Value
<b>Vapour generator conditions—</b>	
SnCl <sub>2</sub> concentration	10% m/v in 20% v/v HCl
SnCl <sub>2</sub> flow rate/ml min <sup>-1</sup>	0.4
HNO <sub>3</sub> concentration	10% v/v HNO <sub>3</sub>
HNO <sub>3</sub> flow rate/ml min <sup>-1</sup>	9.0
Delay time/s	35
Rise time/s	30
Analysis time/min	5
Memory time/s	60
Argon purge gas flow rate/ml min <sup>-1</sup>	50
<b>Amalgam conditions—</b>	
Flush time/s	30
Vaporizer time/s	20
Cooling time/s	90
Argon carrier gas flow rate/ml min <sup>-1</sup>	80
<b>AFS detector conditions—</b>	
Sheath gas flow rate/ml min <sup>-1</sup>	300
Gain	4000
Integration time/s	0.25
Auto zero	ON

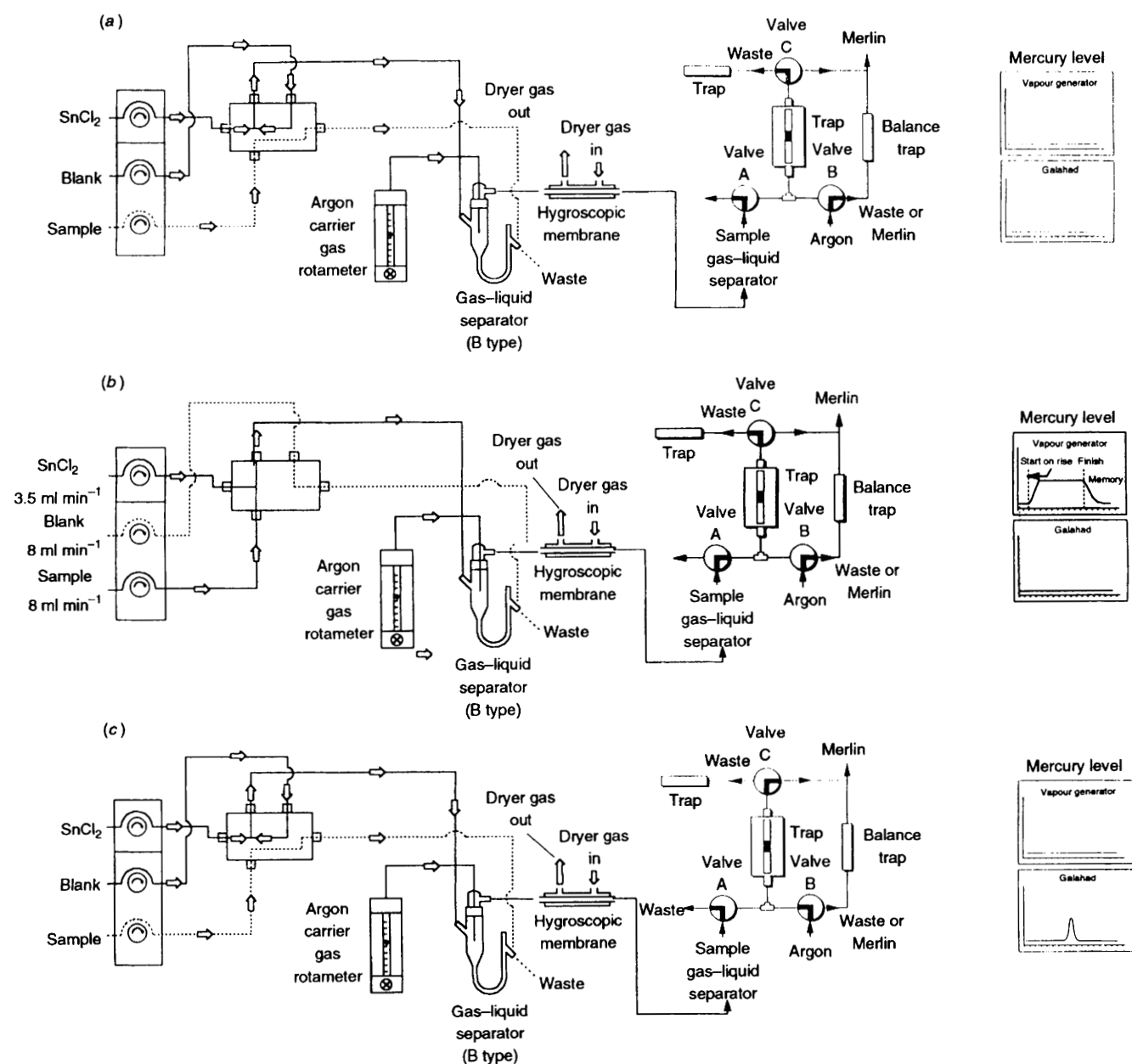
the emission reading. The latter mode compensates for the lamp drift. The detector is described in more detail elsewhere.<sup>13,14</sup>

The amplification of the detector may be varied between 1 and 10000; an amplification of 4000 was selected. Data acquisition time was 0.25 s. Between sample runs the detector was auto-zeroed. The flow rate for the sheath gas, which maintains the mercury in the light path of the detector, was 300 ml min<sup>-1</sup>. Measurements may be expressed in peak height or peak area.

#### Summary of the sequences for the preconcentration and analysis

All the sequences are driven by the microcomputer using the TouchStone software. This allows totally automated preconcentration and analysis. Table 1 summarizes the instrumental conditions used. A summary of the total procedure is outlined as follows. (i) When no sample is being introduced the reductant and the blank are continuously mixed in the gas liquid

separator where the background level is established. During this stage the gold trap is isolated to minimize blank levels. The orientation of the valve manifold is shown in Fig. 2(a). A flow of argon gas is continuously introduced to the fluorescence detector. (ii) The sample is collected from the autosampler via a Teflon probe and flows through the vapour generator for 35 s to ensure complete flush out of any residuals from the previous sample. (iii) When the valve of the vapour generator is activated to introduce the sample, this triggers the valve manifold to the orientation shown in Fig. 2(b). The mercury generated during this stage is preconcentrated on the gold trap. A continuous flow of argon is introduced to the detector at all times. (iv) After preconcentration the vapour generator valve switches back to the reagent blank solution. This process activates the autosampler to stop collecting the sample and switches the valve manifold to that shown in Fig. 2(c). (v) The analysis cycle now starts and TouchStone software begins to acquire data. The detector is auto-zeroed and a baseline is recorded. Residual sample gases are flushed through the system,



**Fig. 2** (a) Schematic diagram of the automated mercury system during non-sampling period (gold trap is isolated to minimize blank levels). (b) Schematic diagram of the automated mercury system during the preconcentration stage. (c) Schematic diagram of the automated mercury system during the measurement period



the gold is heated to release mercury and the trap is cooled rapidly in the chamber. After the coolant cycle has finished the system is ready to collect the next sample.

#### Minimizing contaminations

Mercury-free gas was produced by filtering with a Teflon membrane and a trap consisting of a quartz tube filled with gold-coated sand. In order to minimize the procedural blank, these precautionary measures were combined with the sheltering of the autosampler under a plastic bell-jar. A nitrogen flow ( $50 \text{ ml min}^{-1}$ ), freed of mercury by passing the gas over a gold-coated sand cartridge, was introduced into the jar during the analysis in order to avoid atmospheric contamination. All the plastic tubing, except those of the peristaltic pump of the vapour generator unit, and the vials were Teflon made and acid washed. The tubing for the pump consists of acid ( $\text{HNO}_3$  10%) washed C-Flex silicone rubber. All the Teflon glassware used was soaked for one week in 40%  $\text{HNO}_3$ , rinsed with Milli-Q water, then soaked again for one more week in 10%  $\text{HNO}_3$ . New materials were first washed with detergent or organic solvent, then with a mixture of concentrated  $\text{HCl}$ – $\text{HNO}_3$  (3 + 1, v/v) and rinsed with Milli-Q water prior to the nitric acid cleanings. After being dried under a laminar flow cabinet equipped with HEPA filters, all the materials were bagged in a double polyethylene envelope.

## RESULTS

#### Quality of the Signal

Typical discrete signal profiles were obtained with the system described. The profiles reach a peak maximum within 6 s and show excellent symmetry: results indicate that both peak height and peak area provide equivalent good measurements of the quantity of mercury which passed through the detector.

#### Linearity

The linearity of the detector spans over five orders of magnitude. All calibration curves obtained during the study were found to be linear over the analytical range tested ( $0\text{--}50 \text{ ng l}^{-1}$ ). The sensitivity of the fluorescence detector has to be adjusted to the working concentration range.

#### Sensitivity

The absolute sensitivity obtained with the operating conditions used in this study was  $0.5 \text{ pg}$  of mercury per unit of fluorescence. The units for fluorescence are arbitrary (*i.e.*, % full scale deflection). For a  $45 \text{ ml}$  water sample, and if one takes into account only the instrument noise of the detector, the theoretical detection capacity would be  $0.06 \text{ ng l}^{-1}$ . However, because of the blank level and repeatability the actual limit of detection was slightly higher.

#### Blank assessment

The total blank was quantified to be  $17.8 \text{ pg}$  as the average of eight replicated runs of the reagent blank. These results are reported in Table 2. The argon used as the carrier gas was tested and was  $5.3 \text{ pg}$ , which is 30% of the total blank. The contribution for the reducing agent and the background of the system account for the other 70%. The total blank contribution will vary with the volume of sample taken.

#### Limit of detection

In order to take into account the errors of type I and II at a confident limit of 95%, and assuming the standard deviation

**Table 2** Repeatability of reagent blank

Replicate	Fluorescence unit (%)	Amount of mercury/pg
1	36	18.0
2	37	18.5
3	38	19.0
4	35	17.5
5	34	17.0
6	36	18.0
7	34	17.0
8	34	17.0
Average $\pm s$	$35.5 \pm 1.5$	$17.8 \pm 0.8$

of the sample near the blank is the same as the within-batch standard deviation of the blank ( $s_b$ ), the detection limit is defined as  $4.65 s_b$  by Hewitt<sup>15</sup> *i.e.*,  $4 \text{ pg}$  of mercury. On the basis of results in Table 2, and owing to the volume of sample, the detection limit of the current method was  $0.1 \text{ ng l}^{-1}$ .

#### Repeatability

On the basis of the results in Table 2, the relative standard deviation at  $18 \text{ pg}$  of mercury was 5%.

#### Accuracy

The accuracy or the absence of bias was tested using a Riverine Water reference standard (ORMS-1) provided by the National Research Council of Canada. This material was bottled in Teflon (PFA) at its reception. We obtained  $6.2 \pm 0.3 \text{ ng l}^{-1}$  ( $n=4$ ) for a certified value of  $6.8 \pm 1.3 \text{ ng l}^{-1}$ . The accuracy was also tested by using spikes of inorganic mercury. Within  $0.5\text{--}50 \text{ ng l}^{-1}$ , the recoveries were between 96 and 102%. For taking into account organic mercury present in the natural waters, the samples have to be treated with the appropriate reagent (*e.g.*, Szakacs *et al.*, 1980<sup>16</sup>).

## CONCLUSIONS

Approximately eight samples per hour can be analysed without carryover between samples. The detection limit is improved 20 times over that of the recently proposed automated technique which used atomic absorption spectrophotometry for the detection.<sup>17</sup> The instrumentation is very robust but strict control measures are required to ensure a mercury-free environment around the instrumentation. This greatly affects the quality of the analysis procedures.

The authors would like to thank the following for their assistance and valued input into the project; their continued support is acknowledged; P S Analytical's design and production team and SpinOff Technical Services, UK for software development. This work was partially supported by the Commission of the European Communities (MAST 0053-C/EDB).

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Paper 4/04931D

Received August 11, 1994

Accepted November 23, 1994